VERIFICATION OF TRANSLATION

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[Document Name] DESCRIPTION

[Title of the Invention] METHOD FOR MANUFACTURING LIQUID CRYSTAL DISPLAY, SUBSTRATE FOR LIQUID CRYSTAL DISPLAY AND METHOD FOR MANUFACTURING SUBSTRATE FOR LIQUID CRYSTAL DISPLAY

[Scope of Claims for Patent]

[Claim 1] A method for manufacturing a liquid crystal display, which has a step ejecting a dispersion of spacer particles by an ink-jet device and a step setting a substrate having the spacers located at an arbitrary position and the other substrate having no spacer particle located on the opposite sides via the spacers and the liquid crystal, wherein a color filter comprising a pixel area arrayed in accordance with a given pattern and a shading area defining said pixel area is formed on one of the substrates, as a substrate to be located the spacer particles, a substrate, wherein an orientation layer, a contact angle of which relative to the dispersion of spacer particles is θb, is present in at least an area representing said pixel area on one side of the substrate and an area, a contact angle of which relative to the dispersion of spacer particles is θa, is present at least in a part of an area representing said shading area, and said θa and said θb satisfy $\theta a < \theta b$, is used and the spacer particles are selectively located in the shading area by ejecting a dispersion of spacer particles to a area, a contact angle of which relative to the dispersion of spacer particles is θa, of the substrate.

[Claim 2] A substrate for a liquid crystal display, which is a substrate to be located the spacer particles used by the method for manufacturing a liquid crystal display according to Claim 1, wherein an orientation layer, a contact angle of which relative to the dispersion of spacer particles is θb, is present in at least an area representing said pixel area on one side of the substrate

and, an area, a contact angle of which relative to the dispersion of spacer particles is θa, is present at least in a part of an area representing said shading area, and said θa and said θb satisfy $\theta a < \theta b$.

[Claim 3] A method for manufacturing the substrate for a liquid crystal display according to Claim 2, wherein after an orientation layer, a contact angle of which relative to the dispersion of spacer particles is θb, is uniformly formed on the whole surface of a substrate, by applying non-contact energy irradiation to a position at which the spacer particle is chosen to be locate, the orientation layer in the position applied non-contact energy irradiation is removed or modified to bring a contact angle relative to the dispersion of spacer particles into θa.

[Claim 4] A method for manufacturing the substrate for a liquid crystal display according to Claim 2, wherein a photosensitive polyimide resin precursor or a photosensitive polyimide resin is uniformly applied to a substrate having a surface, a contact angle of which relative to the dispersion of spacer particles is θa, and by exposing via a mask and developing and further heating as needed, an orientation layer comprising polyimide resin is formed in the form of a pattern on the surface of the substrate other than the position at which the spacer particle is chosen to be locate and a contact angle of the surface of said orientation layer relative to the dispersion of spacer particles is brought into θb.

[Detailed description of the invention]

[0001]

[Technical Field]

The present invention relates to a method for manufacturing a liquid crystal display, a substrate for liquid crystal display used by the method for manufacturing a liquid crystal display and a method for manufacturing the substrate for a liquid crystal display.

[0002]

[Background Art]

Currently, a liquid crystal display is widely used to personal computers, portable electronics and the like.

Fig.1 is a sectional view showing an example of a liquid crystal display. As shown in Fig.1, generally, a liquid crystal display has a constitution in which two transparent substrates 1, respectively, on which a transparent electrode 3, an orientation layer 8, a color filter 4 and a black matrix 5 are located inside and a polarizer 2 is located outside, are located on opposed sides through a sealing material 9 installed at the peripheral, and liquid crystal 6 is filled into a gap formed and sealed. And, the transparent substrate 1 is further divided into a pixel area to be a display section provided with a pixel electrode and a shading area not provided with a pixel electrode. In this liquid crystal display, spacer particles 7 are used for the purpose of regulating a spacing of two transparent substrates 1 and maintaining a proper thickness (cell gap) of a liquid crystal layer.

[0003]

As a conventional method for manufacturing a liquid crystal display, there has been used a method for spraying the spacer particles in a random fashion and uniformly on a substrate provided with a pixel electrode. However, in this method, the spacer particles are located also on a pixel electrode, namely, a display section of a liquid crystal display. Generally, since a spacer particle is made of synthetic resin or glass, when a spacer is located on a pixel electrode, there was a problem that a so-called depolarization phenomenon, in which polarized light is disturbed and loses a polarization property, arose and therefore the spacer portion causes light leakage, or orientation of liquid crystal on the spacer surface is

disturbed to cause light leakage and display quality might deteriorate because of degradation of contrast and color tone. Particularly, in a TFT liquid crystal display, a serious problem that a TFT device was damaged when pressure was applied to a substrate might arise.

[0004]

For this problem, attempt has been made to overcome such a problem by locating the spacer particle on an area other than a pixel area which is a display section of a transparent substrate, namely, only in a shading area. For example in Japanese Kokai Publication Hei-4-198919, there is disclosed a method in which after an opening of a mask having an opening and a shading area are oriented, the spacer particles are located only at the position equivalent to the opening. And, in Japanese Kokai Publication Hei-6-258647, there is disclosed a method in which after allowing a photosensitive material to adsorb spacer particles electrostatically, the spacer particles are transferred to a transparent substrate.

[0005]

However, in these methods, since it is necessary to bring a mask or a photosensitive material into contact directly with a substrate, there was a problem that an orientation layer on a substrate might be damaged to cause the degradation of display quality.

[0006]

And, in Japanese Kokai Publication Hei-10-339878, there is disclosed a method in which by spraying charged spacer particles on a pixel electrode of a substrate, to which the voltage of the same polarity is applied, the spacer particles are located on a shading area by virtue of electrostatic repulsive force.

[0007]

However, in this method, there was a problem that because an electrode, which has a configuration along a

pattern to be located, is required, it is impossible to completely locate the spacer particles at arbitrary position and a liquid crystal display of type which this method is applicable to was limited.

[0008]

On the other hand, in Japanese Kokai Publication Sho-57-58124, there is disclosed a method for a liquid crystal display element obtained by being via the spacers and liquid crystal in a gap part between translucent electrode substrates in which a transparent electrode is deposited on the opposed surface, the spacer particles are located and dispersed on a substrate using an ink-jet printer. Since in this method, it was possible to locate a spacer without directly contacting a substrate like the above publication in arbitrary position and in arbitrary pattern, this method was considered to be extremely effective.

[0009]

However, in the method disclosed by the Publication, the problem is that it is impossible to control a size of a droplet ejected by an ink-jet device so as to be smaller than a size of area on which spacers are to be located.

[0010]

Whereas namely, a shading layer (a shading film), wherein the area on which spacers are to be located, called black matrix generically has a width of about 10 to 30 μm, a diameter of a droplet having adhered after a droplet ejected by a ink-jet method has generally adhered to the substrate is about 40 to 200 μm and it is wider than a width of a shading layer.

[0011]

In order to further reduce a size of droplet ejected by an ink-jet device, a diameter of a nozzle hole of the ink-jet device must be reduced, but the diameter of a nozzle hole of a current ink-jet system is about 20 μm at the lowest. Since a particle diameter of the spacer

particle used for the liquid crystal device is about 2 to 10 μm, further the nozzle hole diameter smaller than about 20 μm will result in clogging of a nozzle or unstable ejection and be just not realistic. For this reason, to locate the spacer particles to the non-display area of the liquid crystal device is extremely difficult, considering size accuracy of droplet ejected.

[0012]

As one method for accommodating the droplet ejected by a ink-jet system in a predetermined section (position) accurately, there is studied a method for controlling a wetting property of a predetermined section of a surface receiving the ejection of a droplet with respect to an ejection liquid (droplet). For example, as a ejection liquid of a ink-jet system, an aqueous solution is frequently used, but such an aqueous solution has a characteristic of spreading over a high polar surface receiving the ejection of a droplet, such as a metal surface, with the high polar surface receiving the ejection of a droplet wetted, but not spreading over a low polar surface receiving the ejection of a droplet, such as a resin surface, with the low polar surface receiving the ejection of a droplet wetted.

[0013]

As an example of utilizing such a characteristic, for example in Japanese Kokai Publication Hei-6-347637, there is disclosed a method for using a corresponding ink having a color only in a specified pixel area on a substrate provided with a pixel area and a shading area as a color filter of a liquid crystal display is manufactured. In this method, a water repellent section is formed in a shading area on the substrate by a photoresist method, and it is considered that this method can be applied similarly to the case where the spacer particle is located using a ink-jet system.

[0014]

When the spacer particles are located by using the method, on the substrate of a liquid crystal display, the so-called orientation layer, for example, a polyimide resin film is generally formed in order to regulate an orientation state of liquid crystal and the spacer particles are located on this orientation layer. It is thought, for example, that a coat of photosensitive alkali-soluble resin such as an acrylic acid copolymer and the like is formed on the orientation layer, and by applying photolithography treatment to the coated orientation layer, only the surface of the orientation layer in the position at which the spacer particle is chosen to be located, is brought into a high polar state.

[0015]

However, actually, a rubbing process by nylon or rayon must be applied to the surface of the orientation layer in order to regulate the direction of orientation of liquid crystal and to even the direction of the molecular of the polyimide resin, and it is extremely difficult to apply photolithography treatment to the surface of the orientation layer, thus processed precisely.

[0016]

Further, since the high polar coat exists in convex form on the orientation layer, if the high polar coat is partially formed and then the rubbing process is applied, the high polar coat on the surface of the orientation layer, which is essentially low in adhesion, will peels off and therefore it becomes impossible to locate the spacer particles selectively in the predetermined section. Thus, in actuality, it was technologically difficult to a considerable degree to form an area having the different polarity on the coat of the orientation layer, which needs a special state of the surface.

[0017]

Recently, the liquid crystal display, while a demand of the display quality improvement rises, moves in the direction of widening a pixel area and narrowing a shading area in order to achieve a bright display quality. This moves in the difficult direction locating the spacer particles in the shading area and to the development of a method for effectively locating the spacer particles in the shading area with a high degree of accuracy is strongly desired under the present situation.

[0018]

[Subject which the Invention is to Solve]

In view of the above-mentioned problem and state of art, it is an object of the present invention to provide a method for manufacturing a liquid crystal display, wherein it is possible to locate the spacer particles selectively in a non-display area of the substrate with efficiency and high accuracy and to attain a liquid crystal display which exhibits excellent display quality without the occurrence of a depolarization phenomenon resulting from the spacer particle and the reduction in contrast and color tone due to light leakage, a substrate for a liquid crystal display used by the method for manufacturing a liquid crystal display and a method for manufacturing a substrate for a liquid crystal display.

[0019]

[Means for Solving the Problems]

The present invention as defined in claim 1 pertains to a method for manufacturing a liquid crystal display, which has a step ejecting a dispersion of spacer particles by an ink-jet device and a step setting a substrate having the spacers located at an arbitrary position and the other substrate having no spacer particle located on the opposite sides via the spacers and the liquid crystal, wherein a color filter comprising a pixel area arrayed in accordance with a given pattern and a shading area defining said pixel

area is formed on one of the substrates, as a substrate to be located the spacer particles, a substrate, wherein an orientation layer, a contact angle of which relative to the dispersion of spacer particles is θb, is present in at least an area representing said pixel area on one side of the substrate and an area, a contact angle of which relative to the dispersion of spacer particles is θa, is present at least in a part of an area representing said shading area, and said θa and said θb satisfy θa < θb, is used and the spacer particles are selectively located in the shading area by ejecting a dispersion of spacer particles to a area, a contact angle of which relative to the dispersion of spacer particles is θa, of the substrate. In addition, an area representing a pixel area or an area representing a shading area of the present invention refers to an area lies immediately below the pixel area of a color filter or an area lies immediately below the shading area of a color filter when in a state of being assembled into a liquid crystal display, a display screen is horizontally placed with a substrate surface provided with a color filter up.

[0020]

The present invention as defined in claim 2 pertains to a substrate for a liquid crystal display, which is a substrate to be located the spacer particles used by the method for manufacturing a liquid crystal display according to Claim 1, wherein an orientation layer, a contact angle of which relative to the dispersion of spacer particles is θb, is present in at least an area representing said pixel area on one side of the substrate and, an area, a contact angle of which relative to the dispersion of spacer particles is θa, is present at least in a part of an area representing said shading area, and said θa and said θb satisfy θa < θb.

[0021]

The present invention as defined in claim 3 pertains to a method for manufacturing the substrate for a liquid crystal display according to Claim 2, wherein after an orientation layer, a contact angle of which relative to the dispersion of spacer particles is θb, is uniformly formed on the whole surface of a substrate, by applying non-contact energy irradiation to a position at which the spacer particle is chosen to be locate, the orientation layer in the position applied non-contact energy irradiation is removed or modified to bring a contact angle relative to the dispersion of spacer particles into θa.

[0022]

The present invention as defined in claim 4 pertains to a method for manufacturing the substrate for a liquid crystal display according to Claim 2, wherein a photosensitive polyimide resin precursor or a photosensitive polyimide resin is uniformly applied to a substrate having a surface, a contact angle of which relative to the dispersion of spacer particles is θa, and by exposing via a mask and developing and further heating as needed, an orientation layer comprising polyimide resin is formed in the form of a pattern on the surface of the substrate other than the position at which the spacer particle is chosen to be locate and a contact angle of the surface of said orientation layer relative to the dispersion of spacer particles is brought into θb.

[0023]

The method for manufacturing a liquid crystal display of the present invention can be applied to either a STN type liquid crystal display or a TFT type liquid crystal display. In either type of liquid crystal display, a substrate wherein a transparent electrode and an orientation layer are formed on a substrate is used as a substrate.

[0024]

The above-mentioned STN type liquid crystal display comprises a color filter substrate provided with a color filter and an opposed substrate located on opposite side to the color filter substrate, and the above both substrates have transparent electrodes formed in the form of stripe, and the substrate to be located the spacer particles may be used for any substrate described above.

[0025]

Among the liquid crystal display, the above-mentioned TFT type liquid crystal display comprises a color filter substrate provided with a color filter and an opposed substrate located on opposite side to the color filter substrate, and the opposed substrate generally has an array such as TFT device and referred to as an array substrate. Generally, a contact transparent electrode is formed on the color filter substrate, and a device and the transparent electrode are formed on the array substrate, and the substrate to be located the spacer particles may be used for any substrate described above.

[0026]

The substrate to be ejected the dispersion of spacer particles is not particularly limited and a substrate, used as panel substrates of usual liquid crystal displays, such as a glass plate and a plastic plate can be employed. And, a resin thin film for regulating an orientation of the liquid crystal, referred to as an orientation layer, is generally formed on the surface of the substrate to be ejected the dispersion of spacer particles. Generally, the above orientation layer comprises polyimide resin and controls the orientation of liquid crystal by being subjected to rubbing of the surface. The medium used in the dispersion of spacer particles should not have an orientation layer-contaminating property of penetrating into the orientation layer or dissolving the orientation layer.

[0027]

And, the spacer particles on the substrate may be located on a random basis or may be located at specified positions in specific patterns. The above spacer particles are preferably located in a shading area (non-display area) of the substrate in order to inhibit the reduction in display picture quality resulting from the spacer particle such as light leakage.

[0028]

It is thought that in the above shading area, a shading layer referred to as a black matrix formed around the pixel and a position of a TFT device in a TFT liquid crystal display are formed, but it is preferred to locate the spacer particles in the black matrix portion so as not to break the TFT device. Generally, a width of the black matrix is 10 to 30 μm. The number of spacer particles to be located (particle density) is preferably 50 to 300 per an area of 1 mm square. As far as the spacer particle satisfies the condition of this particle density, it may be located in any part in the black matrix and in any pattern.

[0029]

Usually, an orientation layer comprising a polyimide-based resin is formed by applying a polyimide-based resin precursor and a solution of the precursor or polyimide-based resin solution to the surface of a transparent electrode-formed substrate and a transparent electrode-unformed substrate as an applying method such as a spin coat method as uniform thickness and transforming into the polyimide-based resin by a method such as heating and drying and then subjecting to rubbing so as to give the orientation property of liquid crystal.

[0030]

In an area representing said pixel area, in order to control orientation property, the orientation layer needs to be formed on the surface of a substrate contacting with

a liquid crystal.

[0031]

The essential feature of the method of manufacturing a substrate for a liquid crystal display, wherein the ejected dispersion of spacer particles is selectively spread and wetted over the shading area (non-display area), and then to locate the spacer particles selectively in the shading area by making the surface condition of at least a part of an area representing said shading area different from the surface condition of an area representing said pixel area (display area).

[0032]

Namely, in the method of manufacturing a substrate for a liquid crystal display, like a substrate for a liquid crystal display according to Claim 2, a substrate, wherein an orientation layer, a contact angle of which relative to the dispersion of spacer particles is θb, is present in at least an area representing said pixel area on one side of the substrate and, an area, a contact angle of which relative to the dispersion of spacer particles is θa, is present at least in a part of an area representing said shading area, and said θa and said θb satisfy $\theta a < \theta b$ is used as a substrate to be located the spacer particles. Additionally, in the present invention, a contact angle refers to a static contact angle at a time when after a droplet of an objective liquid (dispersion of spacer particles) is put on a plane, the droplet ceases to spread.

[0033]

In the substrate, when θb and θa do not satisfy a relationship of $\theta a < \theta b$, it becomes impossible to locate the spacer particle selectively in the shading area.

[0034]

The above area having a contact angle of θa may be continuously formed in a line in an area representing the shading area or may be formed in the form of discontinuous

islands having any shape. And, the area having a contact angle of θa is preferably formed in bounds which is smaller than the area representing the shading area and spaced inside the margins of the area representing the shading area. When the area having a contact angle of θa is formed in contact with the margins of the area representing the shading area, an area, in which orientation of liquid crystal is not controlled, overruns out of the area representing the shading area and a area, in which orientation of liquid crystal is not controlled, is generated in an area representing the pixel area, and therefore this may lead to a defect of the display quality of a liquid crystal display.

[0035]

A method for selectively locating the spacer particles at an arbitrary position, while the surface condition of at least a part of an area representing said shading area (a contact angle relative to the dispersion of spacer particles is θa) is different from the surface condition of an area representing said pixel area (a contact angle relative to the dispersion of spacer particles is θb), is not particularly limited and includes, for example, (1) a method in which after an orientation layer is once formed, only the orientation layer in the position, at which the spacer particle is chosen to be locate, is processed afterward by way of removal, modification or coating; and (2) a method for forming an orientation layer only in the position at which the spacer particle is chosen not to be locate. (1) and (2) methods may be used alone, respectively, or may be used in combination of both species.

[0036]

As the above-mentioned (1) method in which after an orientation layer is once formed, only the orientation layer in the position, at which the spacer particle is

chosen to be locate, is processed afterward by way of removal, modification or coating, there is given, for example, like a method for manufacturing the substrate for a liquid crystal display according to Claim 3, a method, wherein after an orientation layer, a contact angle of which relative to the dispersion of spacer particles is θb, is uniformly formed on the whole surface of a substrate, by applying non-contact energy irradiation to a position at which the spacer particle is chosen to be locate, the orientation layer in the position applied non-contact energy irradiation is removed or modified to bring a contact angle relative to the dispersion of spacer particles into θa.
In the method for manufacturing the substrate for a liquid crystal display of the present invention, it is preferred that an orientation layer is first formed, and by applying rubbing treatment to the surface of this orientation layer, the orientation of liquid crystal is controlled, and then non-contact energy is irradiated to a position at which the spacer particle is chosen to be located.

[0037]

A method for the above-mentioned irradiation of non-contact energy is not particularly limited as long as it can converge a beam diameter of the energy irradiation so as to be 20 μm or less and cause an orientation layer material such as polyimide-based resin to decompose, vaporize, burn and oxidize and any method can be employed, but for example, laser irradiation, excimer laser irradiation, corona discharge treatment and low temperature plasma treatment are given. In accordance with these method for the irradiation of non-contact energy, since the orientation layer can be removed or modified without contacting the surface of the orientation layer after the orientation of liquid crystal is controlled by previously applying rubbing treatment to the surface of the

orientation layer, an orientation layer, in which orientation of liquid crystal is controlled, cam be relatively easily obtained. These method for the irradiation of non-contact energy may be used alone or may be used in combination of two or more species.

[0038]

And, the method for coating only the position, at which the spacer particle is chosen to be locate, with the orientation layer is not particularly limited but includes, among others, a method for forming a heterogeneous film on the surface of the orientation layer by treatment techniques such as vapor deposition through the medium of a mask, sputtering, CVD (Chemical Vapor Deposition) and plasma polymerization. These treatment techniques may be used alone or may be used in combination of two or more species.

[0039]

As the (2) method for forming an orientation layer only in the position at which the spacer particle is chosen not to be locate, there is given, for example, like a method for manufacturing the substrate for a liquid crystal display according to Claim 4, a method, wherein a photosensitive polyimide resin precursor or a photosensitive polyimide resin is uniformly applied to a substrate having a surface, a contact angle of which relative to the dispersion of spacer particles is θa, and by exposing via a mask and developing and further heating as needed, an orientation layer comprising polyimide resin is formed in the form of a pattern on the surface of the substrate other than the position at which the spacer particle is chosen to be locate and a contact angle of the surface of said orientation layer relative to the dispersion of spacer particles is brought into θb. This method can be conducted, for example as the method according to "Polyfile 2, 14-29 (1990) (published by

TAISEISYA LTD.) ”.

[0040]

Though this method needs to apply rubbing treatment to the whole surface of a substrate after an orientation layer in the form of a pattern is once formed on the substrate, it has an advantage that even though rubbing treatment is applied after the orientation layer comprising polyimide resin is coated with a high polar film, a problem of peeling of the high polar film does not arise.

[0041]

And, an orientation layer comprising polyimide resin may be formed by depositing a polyimide resin precursor only on an area requiring an orientation layer on the substrate via a mask provided with a pattern having openings corresponding to areas intended for the formation of the orientation layer by treatment techniques such as vapor deposition, sputtering, CVD and plasma polymerization.

[0042]

The above-mentioned spacer particle composing a dispersion of spacer particles used in the method for manufacturing a liquid crystal display of the present invention is not particularly limited and may be, for example, an inorganic-based particle such as a silica-based particle and an organic-based particle such as an organic polymer-based particle. The inorganic-based particle and organic-based particle may be used alone or may be used in combination of two or more species.

[0043]

In the invention, among the inorganic-based particle and organic-based particle, the organic-based particle is preferred in that it has adequate hardness not to damage an orientation layer formed on a substrate of a liquid crystal display and is easy to follow the change in thickness due to thermal expansion or thermal contraction of the orientation layer, and further is relatively less in move

within a cell.

[0044]

It is preferred that the composition of the monomer for obtaining the organic polymer-based particle is the mixed monomer obtained by polymerizing a monofunctional monomer and a polyfunctional monomer since the organic polymer-based particle having enough strength. The content of the above-mentioned polyfunctional monomer in the mixed monomer is preferably 30% by weight or less. When it is more than 30% by weight, strength and hardness of the obtained organic polymer-based particle may be too high.

[0045]

The above-mentioned monofunctional monomer is not particularly limited and includes, for example, styrene derivatives such as styrene, α-methylstyrene, p-methylstyrene, p-chlorostyrene and chloromethylstyrene; vinyl esters such as vinyl chloride, vinyl acetate and vinyl propionate; unsaturated nitriles such as acrylonitrile; (meth)acrylate ester derivatives such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, stearyle (meth)acrylate, ethylene glycol (meth)acrylate, trifluoroethyl (meth)acrylate, pentafluoropropyl (meth)acrylate and cyclohexyl (meth)acrylate. These monofunctional monomers may be used alone or may be used in combination of two or more species. In the present invention, "(meth)acryl" means "acryl" or "methacryl".

[0046]

The above-mentioned polyfunctional monomer is not particularly limited and includes, for example, divinylbenzene; diallyl phthalate; triallyl isocyanurate; 1,6-hexanediol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, tetramethylolmethane tri(meth)acrylate, tetramethylolpropane tetra(meth)acrylate, trimethylolpropane tri(meth)acrylate and derivatives

thereof, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, polytetramethylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 1,3-butylene glycol di(meth)acrylate; polyethylene glycol di(meth)acrylates such as ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate; polypropylene glycol di(meth)acrylates such as propylene glycol di(meth)acrylate; 2,2-bis [4-(acryloxypolyalkoxy) phenyl] propane di(meth) acrylates such as 2,2-bis[4-(methacryloxypolyethoxy)phenyl]propane di(meth)acrylate of 2,2-bis[4-(methacryloxyethoxy)phenyl]propane di(meth)acrylate, 2,2-hydrogenated bis[4-(acryloxypolyethoxy)phenyl]propane di(meth)acrylate and 2,2-bis[4-(acryloxyethoxypolypropoxy)phenyl]propane di(meth)acrylate. These polyfunctional monomers may be used alone or may be used in combination of two or more species.

[0047]

A method for producing the organic polymer-based particle by polymerizing the above-mentioned monomer or preferably the mixed monomer obtained by polymerizing a monofunctional monomer and a polyfunctional monomer is not particularly limited and for example, suspension polymerization, seed polymerization, and dispersion polymerization are given.

[0048]

Among the method for producing, since the suspension polymerization can obtain polydisperse particles having a relatively wide particle size distribution, it is suitable for the aim of producing the particle including a wide variety of particle diameter. But, if the particle produced by the suspension polymerization is used as a spacer particle, the particle having a desired particle diameter and particle diameter distribution by conducting a

classification operation is preferably used. Additionally, since the seed polymerization and dispersion polymerization can obtain monodisperse particles without conducting a classification operation, it is suitable for the aim of producing the spacer particle having a specified particle diameter in large quantity.

[0049]

In the case of the polymerization, a medium and initiator are used.

[0050]

The medium is appropriately determined depending on kinds and compositions of a monomer to be used, for example, water; alcohols such as methanol, ethanol, propanol; cellosolves such as methyl cellosolve, ethyl cellosolve, ketones such as acetone, methyl ethyl ketone, methyl butyl ketone, 2-butanone; acetates such as ethyl acetate, butyl acetate; hydrocarbons such as acetonitrile, N,N-dimethylformamide, dimethyl sulfoxide. The medium may be used alone or may be used in combination of two or more species.

[0051]

The above-mentioned initiator is not particularly limited and for example, organic peroxides such as benzoyl peroxide, lauroyl peroxide, o-chlorobenzoyl peroxide, o-methoxybenzoyl peroxide, 3,5,5-trimethylhexanoyl peroxide and t-butylperoxy-2-ethylhexanoate and di-t-butyl peroxide; and azo compounds such as azobis(isobutyronitrile), azobis(cyclohexacarbonitrile) and azobis(2,4-dimethylvaleronitrile) are given. These initiators may be used alone or may be used in combination of two or more species.

[0052]

Preferably, an amount of the above initiator to be used is not particularly limited and is usually 0.1 to 10 parts by weight per 100 parts by weight of the monomer.

When it is less than 0.1 parts by weight per 100 parts by weight of the monomer, the polymerization reaction may be insufficient, and on the other hand, when it is more than 10 parts by weight per 100 parts by weight of the monomer, the molecular weight of the organic polymer-based particle to be obtained may be too low.

[0053]

The above-mentioned suspension polymerization is a method, in which a monomer composition comprising a polymerizable monomer and an initiator is dispersed in a poor solvent so as to give an intended particle diameter and polymerized. As a medium (poor medium) used for the above suspension polymerization, there is usually used a substance formed by adding a disperse stabilizer to water. As the above-mentioned disperse stabilizer, there are given polymers soluble in a medium such as polyvinyl alcohol, polyvinylpyrrolidone, methyl cellulose, ethyl cellulose, polyacrylic acid, polyacrylamide and poly(ethylene oxide). And, a surfactant such as a nonionic surfactant, anion surfactant, cation surfactant and ampholytic surfactant is also appropriately used. These disperse stabilizer may be used alone or may be used in combination of two or more species.

[0054]

The conditions of polymerization of the above-mentioned suspension polymerization vary with species of the initiator and the polymerizable monomer, but usually, suitably, polymerization temperature is 50 to 80°C and polymerization time is 3 to 24 hours.

[0055]

The above-mentioned seed polymerization is a method in which by allowing the monodisperse seed particle synthesized by soap-free polymerization or emulsion polymerization to absorb further a polymerizable monomer and polymerizing this seed particle, a particle diameter of

the particle is expanded to a predetermined diameter. A monomer used in producing the above seed particle is not particularly limited, but it is preferred to use a substance having components close to that of a monomer in conducting seed polymerization in order to inhibit phase separation. For example, styrene, a styrene derivative and the like are preferred, since monodisperse property of the particle size distribution is fine.

[0056]

Since a particle size distribution of the seed particle is reflected on a particle size distribution after seed polymerization, it is preferably as monodisperse as possible and CV value ((the standard deviation of the particle diameter / the average particle diameter)×100) is preferably 5% or less. A monomer to be absorbed in the above seed particle in seed polymerization is preferred to use a substance having components close to that of a monomer in conducting seed polymerization in order to inhibit phase separation. For example, when the seed particle comprises a styrene-based resin, the monomer to be absorbed in the above seed particle is preferred for an aromatic divinyl monomer and when the seed particle comprises an acryl-based resin, the monomer to be absorbed in the above seed particle is preferred for an acrylic multivinyl monomer.

[0057]

In seed polymerization, it is preferred to add 20 to 100 parts by weight of a polymerizable monomer per 1 part by weight of seed particles. When the addition amount is less than 20 parts by weight, the strength of the spacer particle to be obtained may become insufficient, and when it is more than 100 parts by weight, a particle size distribution may widen due to particle cohesion during seed polymerization.

[0058]

And, in seed polymerization, a disperse stabilizer may also be used as required. As such a disperse stabilizer, polymers soluble in water are suitable such as polyvinyl alcohol, polyvinylpyrrolidone, methyl cellulose, ethyl cellulose, polyacrylic acid, polyacrylamide and poly(ethylene oxide) are given. And, a surfactant such as a nonionic surfactant, anion surfactant, cation surfactant and ampholytic surfactant is also appropriately used. These disperse stabilizer may be used alone or may be used in combination of two or more species.

[0059]

The above-mentioned dispersion polymerization is a method, in which by conducting polymerization in a poor solvent system which dissolves a polymerizable monomer but does not dissolve a polymer produced and adding a polymer-based disperse stabilizer to this system, a produced polymer is precipitated in the form of particle.

[0060]

In dispersion polymerization, generally, when a monomer comprising a polyfunctional monomer is used, the cohesion of the resulting particle is apt to occur and it is difficult to obtain monodisperse crosslinked particles stably, but it becomes possible to stably polymerize a monomer containing a crosslinked component by selecting conditions.

[0061]

The amount of the polyfunctional monomer in the monomer comprising the polyfunctional monomer is not particularly limited and but, from the viewpoint of cohesion during polymerization or strength of the obtained polyfunctional polymer, is preferably 50% by weight or more with respect to the total monomers. When the amount of the polyfunctional monomer in the monomer comprising the polyfunctional monomer is less than 50% by weight, since the surface of particle formed during polymerization is

soft in the medium, impingement between the fine particles causes cohesion and therefore a particle size distribution widens, and further this may result in cohesion body. And, even though monodispersity is retained, it may be difficult to attain adequate fracture strength as a spacer particle when a crosslinking density is low.

[0062]

Since the above-mentioned spacer particle composing a dispersion of spacer particles used in the present invention is used as a spacer particle (gap material), the above-mentioned inorganic-based particle or organic-based particle composing the spacer particle (hereinafter referred to as "inorganic-based particle or organic-based particle" or simply "particle") and the finally obtained spacer particle preferably have certain strength.

[0063]

In the case of adopting compressive modulus of elasticity at 10% deformation (10% K value) as an indicator of compressive strength of the particle and space particle, the above-mentioned spacer particle of the liquid crystal device is not particularly limited and preferably has compressive modulus of elasticity (10% K value) of the particle and space particle of 2000 to 15000 MPa.

[0064]

When the compressive modulus of elasticity is less than 2000 MPa, the spacer particle may be deformed by press pressure in assembling a liquid crystal display and therefore a proper gap may not be maintained. When it is more than 15000 MPa, the spacer particle may damage an orientation layer on the substrate to cause display anomalies in incorporating it in a liquid crystal display.

[0065]

In addition, the compressive modulus of elasticity (10% K value) means the value by measuring to correctly-understand hardness of the particle and space particle in

the following manner.

(Measuring method of compressive modulus of elasticity (10% K value))

the above 10% K value can be determined, for example, by using Micro Compression Testing Machine (PCT-200 manufactured by SHIMADZU CORPORATION) according to Japanese Kouhyou Publication Hei-6-503180 and measuring the load which deforms the fine particle by 10% with a flat end face of a diamond column of 50 μm in diameter.

[0066]

The above particle and spacer particle may be colored in order to improve contrast of a liquid crystal display.

[0067]

As a method for coloring the above particle and spacer particle, there are given, for example, a method for containing carbon black, disperse dye, acid dye, basic dye and metal oxide; and a method in which an organic film is formed on the surface of particle and spacer particle and this film is decomposed or carbonized at elevated temperatures. Further, when a material, composing a particle and spacer particle, itself has a color, it may be used as is without coloring.

[0068]

The above-mentioned spacer particle composing a dispersion of spacer particles used in the present invention is not particularly limited, on the surface of a particle, there may be formed a surface coating layer formed by chemically combining securely a vinyl-based thermoplastic resin, formed by polymerizing vinyl-based monomers, with the surface of a particle through graft polymerization.

[0069]

The vinyl-based monomer composing the above vinyl-based thermoplastic resin is not particularly limited and includes, for example, vinyl-based monomers having hydroxyl

group such as 2-hydroxyethyl (meth)acrylate, 1,4-hydroxybutyl (meth)acrylate, (poly)caprolactone-modified hydroxyethyl (meth)acrylate, allyl alcohol and glycerin mono allyl ether; acrylic acids and α-alkyl derivatives or β-alkyl derivatives thereof such as (meth)acrylic acid, α-ethyl acrylic acid and crotonic acid; unsaturated dicarboxylic acids such as fumaric acid, maleic acid, citraconic acid and itaconic acid; vinyl-based monomers having carboxylic groups such as derivatives of mono-2-(meth)acryloyloxyethyl ester of the above unsaturated dicarboxylic acids; vinyl-based monomers having a sulfonyl group such as t-butylacrylamidesulfonic acid, styrenesulfonic acid and 2-acrylamido-2-methyl propane sulfonic acid; vinyl-based monomers having a phosphonyl group such as vinyl phosphate and 2-(meth)acryloyloxyethyl phosphate; vinyl-based monomers having an amino group like amines having acryloyl groups such as dimethylaminoethyl methacrylate and diethylaminoethyl methacrylate; vinyl-based monomers having ether groups such as terminal alkyl ether of (poly)ethylene glycol (meth)acrylate, terminal alkyl ether of (poly)propylene glycol (meth)acrylate and tetrahydrofurfuryl (meth)acrylate; vinyl-based monomers having an amide group such as (meth)acrylamide, methylol(meth)acrylamide and vinylpyrrolidone; (meth)acrylate esters such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, i-propyl (meth)acrylate, n-butyl (meth)acrylate, i-butyl (meth)acrylate, t-butyl (meth)acrylate, cyclohexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, stearyle (meth)acrylate, isostearyle (meth)acrylate, isodecyl (meth)acrylate, tridecyl (meth)acrylate, isobornyl (meth)acrylate, phenyl (meth)acrylate, benzil (meth)acrylate, methyl-α-chloro (meth)acrylate and glycidyl (meth)acrylate; unsaturated nitriles such as acrylonitrile and methacrylonitrile;

maleimides such as phenylmaleimide and cyclohexylmaleimide; vinyl esters such as vinyl acetate and vinyl propionate; vinyl ethers such as ethyl vinyl ether and butyl vinyl ether; vinyl halides such as vinyl chloride and vinyl bromide; vinyl-based monomers, each of which has at least one polymerizable unsaturated double bond in a molecule, such as olefins like ethylene, propylene, 1-butene, 2-butene and butadiene, and styrene and derivatives thereof like styrene and α-methylstyrene. These vinyl-based monomers may be used alone or may be used in combination of two or more species.

[0070]

By chemically combining securely a vinyl-based thermoplastic resin formed by polymerizing vinyl-based monomers with the surface of the particle via graft polymerization, a spacer particle having a surface coating layer comprising a vinyl-based thermoplastic resin on the surface can be obtained.

[0071]

The surface coating layer obtained by this method is preferred because of the less occurrence of problems such as peeling or elution of the surface coating layer in ink of ink-jet method or a cell of a liquid crystal display. Among them, for example, the method of forming the surface coating layer comprising a vinyl-based thermoplastic resin on the surface by generating a radical to react an oxidizer with a particle having a reducing group on the surface and graft-polymerizing to originate this radical according to the method disclosed in Japanese Kokai Publication Hei-11-223821 is preferred since the surface coating layer having high density and sufficient thickness can be obtained.

[0072]

The dispersion of spacer particles used in the present invention, wherein the above-mentioned spacer particle is dispersed in a medium.

[0073]

The above-mentioned medium is not particularly limited as long as being liquid at room temperature and can be dispersing the spacer particles, among others, water or hydrophilic liquid is preferred.

[0074]

Generally, an ink-jet system trends to be able to eject a liquid stably in the case of using water or hydrophilic liquid as a medium. When a highly hydrophobic organic solvent is used as the medium, the medium may affect a member composing a head or may elute a part of adhesives, which bond the member. Consequently the above-mentioned medium of dispersion of spacer particles is preferably water or a hydrophobic organic solvent.

[0075]

The water is not particularly limited and includes, for example, ion-exchange water, pure water, groundwater, running water, industrial water. The water may be used alone or may be used in combination of two or more species.

[0076]

As the above-mentioned hydrophobic organic solvent, there are given, for example, in addition to water, monoalcohols such as ethanol, n-propanol, 2-propanol, 1-butanol, 2-butanol, 1-methoxy-2-propanol, furfuryl alcohol, tetrahydrofurfuryl alcohol, and the like; polymers of ethylene glycol such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, and the like; polymers of propylene glycol such as propylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, and the like; lower monoalkyl ethers such as monomethyl ether, monoethyl ether, monoisopropyl ether, monopropyl ether and monobutyl ether of propylene glycol and polymers of propylene glycol, respectively; lower dialkyl ethers such as dimethyl ether, diethyl ether, diisopropyl ether, dipropyl ether of propylene glycol and

polymers of propylene glycol, respectively; alkyl esters such as monoacetate, diacetate of propylene glycol and polymers of propylene glycol, respectively; diols such as 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 3-methyl-1,5-pentanediol, 3-hexene-2,5-diol, 1,5-pentanediol, 2,4-pentanediol, 2-methyl-2,4-pentanediol, 2,5-hexanediol, 1,6-hexanediol, neopentyl glycohol, and the like; ether derivatives of diols; acetate derivatives of diols; polyhydric alcohols or ether derivatives thereof such as glycerin, 1,2,4-butanetriol, 1,2,6-hexanetriol, 1,2,5-pentanetriol, trimethylol propane, trimethylol ethane, pentaerythritol, and the like; acetate derivatives of polyhydric alcohols; dimethyl sulfoxide, thiodiglycol, N-methyl-2-pyrrolidone, N-vinyl-2-pyrrolidone, γ-butyrolactone, 1,3-dimethyl-2-imidazolidine, sulfolane, formamide, N,N-dimethylformamide, N,N-diethylformamide, N-methylformamide, acetamide, N-methylacetamide, α-terpineol, ethylene carbonate, propylene carbonate, bis(β-hydroxyethyl)sulfone, bis(β-hydroxyethyl) urea, N,N-diethylethanolamine, abietynol, diacetone alcohol and urea. These water and hydrophobic organic solvent may be used alone or may be used in combination of two or more species.

[0077]

The medium preferably contains a hydrophilic organic solvent having a boiling point of less than 100°C. More preferably, the medium contains a hydrophilic organic solvent having a boiling point of 70°C or more and less than 100°C. In the present invention, "a boiling point" means a boiling point at an atmospheric pressure of 1 atm.

[0078]

As such a hydrophilic organic solvent having a boiling point of less than 100°C, it is not particularly limited and given lower monoalcohols such as ethanol, n-propanol, 2-propanol and the like, and acetone. These hydrophilic organic solvent having a boiling point of less

than 100°C may be used alone or may be used in combination of two or more species.

[0079]

The hydrophilic organic solvent having a boiling point of less than 100°C volatilizes at relatively low temperature as the dispersion of spacer particles is evaporated after being ejected onto the substrate. If the medium contacts with an orientation layer at high temperature, drying temperature cannot be set high, since the picture quality of display of a liquid crystal display may be impaired by contaminating the orientation layer. Accordingly, the hydrophilic organic solvent having a boiling point of less than 100°C is preferably used. However if the hydrophilic organic solvent having a boiling point of less than 100°C is apt to volatilize at room temperature, since it is apt to produce the cohesion of spacers in the case of preparing or preserving the dispersion of spacer particles and the dispersion of spacer particles adjoining the nozzle of the ink-jet system becomes apt to evaporate and therefore an ejecting property of the ink-jet may be impaired, the hydrophilic organic solvent apt to volatilize at room temperature is not preferably used.

[0080]

In addition, the hydrophilic organic solvent having a boiling point of less than 100°C, it is not particularly limited and but preferably has the surface tension of 25 mN/m or less at 20°C. Generally, an ink-jet system exhibits good ejection accuracy when the surface tension of a liquid to be ejected is 30 to 50 mN/m. On the other hand, when the surface tension of a droplet of the dispersion ejected onto a substrate is high, it is easier to move the spacer particle in the drying process.

[0081]

When the surface tension of the hydrophilic organic

solvent having a boiling point of less than 100°C is 25 mN/m or less, at the moment when the dispersion is ejected, the surface tension of the dispersion of spacer particles can be set relatively low and therefore good ejection accuracy is attained, and on the other hand after the moment when the dispersion adheres to the substrate, since the liquid volatilizes faster than another components in the dispersion of spacer particles, the surface tension of the dispersion becomes large and therefore the spacer becomes apt to move in the drying process.

[0082]

The content of the above-mentioned hydrophilic organic solvent having a boiling point of less than 100°C in the medium is preferably 10 to 80% by weight.

[0083]

When this content of the hydrophilic organic solvent having a boiling point of less than 100°C is less than 10% by weight, efficiency containing the hydrophilic organic solvent having a boiling point of less than 100°C may not be obtained, and when this content of the hydrophilic organic solvent having a boiling point of less than 100°C is more than 80% by weight, the dispersion of spacer particles adjoining the nozzle of the ink-jet system becomes apt to evaporate in preparing the dispersion of spacer particles or in a tank and therefore the possibility of producing cohesion spacers increases and an ejecting property and accuracy of the ink-jet may be impaired.

[0084]

Preferably, the medium contains a hydrophilic organic solvent having a boiling point of 150°C or more. More preferably, the medium contains a hydrophilic organic solvent having a boiling point of 150°C or more and 200°C or less.

[0085]

As such a hydrophilic organic solvent having a

boiling point of 150°C or more, there are given ethers of lower alcohol such as ethylene glycol, ethylene glycol monomethyl ether, ethylene glycol dimethyl ether and the like. These hydrophilic organic solvent having a boiling point of 150°C or more may be used alone or may be used in combination of two or more species.

[0086]

The above-mentioned hydrophilic organic solvent having a boiling point of 150°C or more inhibits the dispersion of spacer particles from evaporating in preparing and storing the dispersion of spacer particles to produce cohesion spacers and prevents the dispersion of spacer particles from evaporating excessively in the neighborhood of the nozzle of the ink-jet system to reduce the ejection accuracy and ejection property.

[0087]

Preferably, the above-mentioned hydrophilic organic solvent having a boiling point of 150°C or more has the surface tension of 30 mN/m or more at 20°C. When the surface tension of the liquid having a boiling point of 150°C or more is 30 mN/m or more, after the moment when a droplet of the dispersion of spacer particles adheres to the substrate, the water or hydrophilic organic solvent having a lower boiling point volatilizes and then the surface tension of the dispersion of spacer particles is kept high and therefore the spacer becomes apt to move.

[0088]

The content of the above-mentioned hydrophilic organic solvent having a boiling point of 150°C or more in the medium is not particularly limited and but preferably 10 to 80% by weight.

[0089]

When this content of the above-mentioned hydrophilic organic solvent having a boiling point of 150°C or more in the medium is less than 10% by weight, the effect due to

containing the hydrophilic organic solvent having a boiling point of 150°C or more may be insufficient, and when it is more than 80% by weight, it takes significantly much time to dry and therefore production efficiency is reduced and in addition to this the degradation of the display picture quality of a liquid crystal display due to the ontamination of an orientation layer becomes apt to occur.

[0090]

The solid content of spacer particles in dispersion of spacer particles used in the present invention is not particularly limited and but preferably 0.05 to 5% by weight and more preferably 0.1 to 2% by weight.

[0091]

When the solid content of spacer particles in dispersion of spacer particles is less than 0.05% by weight, effective dose of the spacer particle may not be contained in an ejected droplet of the dispersion of spacer particles, and when it is more than 5% by weight, a nozzle of an ink-jet system may become apt to clog or numbers of spacer particles contained in the ejected droplet of dispersion of spacer particles having adhered becomes too many and therefore the spacer particle may become less prone to move in the drying processs.

[0092]

In the dispersion of spacer particles, the above-mentioned spacer particles are preferably dispersed in the form of a single particle in the medium. When the spacer particles are not dispersed in the form of a single particle in the medium, cohesion particles are present in the dispersion of spacer particles, not only they cause the reduction in ejection accuracy, but also they might cause clogging of a nozzle of an ink-jet system in an extreme case.

[0093]

The above dispersion of spacer particles used in the

present invention may also contain one species or two or more species of various additives such as a tackifier, a viscous regulator, a pH regulator, a surfactant, an antifoamer, an antioxidant, a heat stabilizer, a light stabilizer, an ultraviolet absorber and a coloring agent as required to the extent that achievement of the issues of the present invention is not inhibited.

[0094]

A method for ejecting the dispersion of spacer particles onto the substrate is not particularly limited and but may carry out the following method.

[0095]

As an ink-jet system, there can be used a system employing a publicly known method such as a piezo method in which liquid is ejected by vibrations of a piezoelectric element, a thermal method in which liquid is ejected with the aid of the expansion of liquid by rapid heating and a bubble-jet method (registered trademark) in which liquid is ejected from nozzles by rapid heating the heater element.

[0096]

A diameter of a nozzle hole of the above-mentioned ink-jet system is preferably 20 to 100 μm. If the nozzle hole diameter is less than 20 μm, when the dispersion of spacer particles having a particle diameter of 2 to 10 μm is ejected, ejection accuracy is reduced due to the too small difference between the nozzle hole diameter and the particle diameter, and extremely, the ejection of the dispersion of spacer particles may become impossible due to nozzle clogging. When it is more than 100 μm, the precision of locating spacers may become rough since the ejected liquid droplet becomes large and therefore the diameter of a droplet (adhered diameter) having adhered also becomes large.

[0097]

A droplet diameter of the dispersion of spacer

particles ejected from the nozzle of the above-mentioned ink-jet system is preferably 10 to 80 μm. As a method for controlling the droplet diameter is not limited, there is given, for example, a method for optimizing the diameter of a nozzle hole or a method for optimizing electrical signals controlling the ink-jet system. The latter is especially important in the case where an ink-jet system of a piezo ink-jet method is employed.

[0098]

A diameter of an adhered droplet to the substrate is preferably 30 to 150 μm. When the diameter is less than 30 μm, the diameter of a nozzle hole must be very small, and therefore a problem arises in terms of nozzle clogging with spacer particles and machining accuracy of a nozzle. When it is more than 150 μm, the precision of locating spacers may become rough.

[0099]

A method for drying the medium in the adhered droplet of the dispersion of spacer particles on the substrate is not particularly limited and but may carry out the following method.

[0100]

In the case of drying, it is preferable to be dried with inhabiting the spacer particles in a circle of the diameter that is smaller than the diameter of the droplet of the dispersion of spacer particles, after the dispersion of spacer particles ejected from the nozzle of the ink-jet system to the substrate is dried.

[0101]

In order to gather the spacer particles in the vicinity of a central portion of the adhered droplet of the dispersion of the spacer particles in the drying process, it becomes important to set the boiling point of the medium, a drying temperature, a drying time, the surface tension of the medium, the contact angle of the medium relative to the

orientation layer and the concentration of the spacer particle at favorable conditions, especially, the drying condition becomes important.

[0102]

It is preferred to dry in a certain degree of duration in such a way that the medium does not disappear during the spacer particles move on the substrate. Accordingly, the condition of evaporating the medium rapidly is not preferred. The condition of drying at a high temperature for a long time is not preferred, since, if the medium contacts an orientation layer at elevated temperatures for a long time, this may cause the contamination of an orientation layer to impair the picture quality of the liquid crystal display. The medium being apt to volatilize at room temperature is not preferred, since the dispersion of spacer particles adjoining the nozzle of the ink-jet system becomes apt to evaporate, and therefore an ejecting property of the ink-jet may be impaired and cohesion spacers may be produced in preparing the dispersion of spacer particles or due to evaporation in a tank. Furthermore, the condition of drying at a low temperature for a long time is not preferred, since the productivity of the liquid crystal display falls, if the drying time gets longer, even if the surface temperature of the substrate is a comparatively low condition.

[0103]

Considering these limiting conditions, as preferred conditions of drying, there is given, for example, that the surface temperature of a substrate at the time when the dispersion of spacer particles adheres to the substrate is preferably at least 20°C lower than a boiling point of a medium component having the lowest boiling point among mediums contained in the dispersion.

[0104]

When the surface temperature of a substrate is less

than 20°C lower than a boiling point of a medium component having the lowest boiling point among mediums contained in the dispersion, not only the medium component having the lowest boiling point is rapidly volatilized and therefore the spacer particles cannot move in the drying process, but also in an extreme case, the whole droplet moves around on the substrate due to a rapid boil of the liquid and therefore the precision of locating spacers may significantly deteriorates.

[0105]

And, in the drying method wherein the medium volatilizes with increasing the surface temperature of the substrate by little and little after the dispersion of spacer particles is adhered to the substrate, the surface temperature of the substrate at the time when the droplet of the dispersion of spacer particles is adhered to the substrate is not particularly limited and but is preferably a temperature at least 20°C lower than a boiling point of a medium having the lowest boiling point among mediums contained in the dispersion of the spacer particles, and the surface temperature of the substrate until the completion of drying is 90°C or less, and is preferably 70°C or less.

[0106]

When the surface temperature of a substrate is a temperature lower than a boiling point of a medium having the lowest boiling point by 20°C, not only the medium having the lowest boiling point is rapidly volatilized and therefore the spacer particles cannot move, but also in an extreme case, the whole droplet moves around on the substrate due to a rapid boil of the medium and therefore the precision of locating spacers may significantly deteriorates. When the surface temperature exceeds 90°C, this may cause the contamination of an orientation layer and picture quality of display of a liquid crystal display

may be impaired. Incidentally, in the present invention, the completion of drying refers to a time when a droplet on a substrate disappears.

[0107]

A desired liquid crystal display can be manufactured by bonding a substrate located spacer particles selectively and an opposed substrate and a peripheral sealing material and pressing against to each other under heating, and filling liquid crystal into the gap formed between these substrates.

[0108]

[operation]

If the method for manufacturing a liquid crystal display of the present invention is used, since an orientation layer, a contact angle of which relative to the dispersion of spacer particles is θb, is present in at least an area representing said pixel area on one side of the substrate and an area, a contact angle of which relative to the dispersion of spacer particles is θa, is present at least in a part of an area representing said shading area, the substrate wherein said θa and said θb satisfy a relationship $\theta a < \theta b$ is used and the dispersion of spacer particles is ejected onto the area where a contact angle relative to the dispersion of spacer particles is θa with an ink-jet system, it is possible to locate the spacer particles selectively in a non-display area of the substrate with efficiency and high accuracy and to attain a liquid crystal display which exhibits excellent display quality without the occurrence of a depolarization phenomenon resulting from the spacer particle and the reduction in contrast and color tone due to light leakage.

[0109]

[Embodiments]

Hereinafter, the present invention will be described in more detail by way of examples, but the present

invention is not limited to these examples.

[0110]

(1) Preparation seed particles of spacer particles

To a separable flask, 15 parts by weight of divinylbenzene, 5 parts by weight of isooctyl acrylate and 1.3 parts by weight of benzoyl peroxide as an initiator were charged and mixed uniformly. Next, to this mixture, 20 parts by weight of a 3% by weight aqueous solution of polyvinyl alcohol (trade mark "KURARAY Poval GL-03" made by KURARAY CO., LTD.) and 0.5 parts by weight of sodium dodecyl sulfate were charged and stirred uniformly, and then 140 parts by weight of ion-exchanged water was added. Then, this mixed aqueous solution was polymerized at 80°C for 15 hours under nitrogen flow while being stirred to obtain fine particles. The obtained fine particles were adequately washed with hot water and acetone, and then classified and the acetone was volatilized to obtain seed particles of spacer particles. An average particle diameter of the obtained spacer particles was 5 μm and a CV value was 3.0%.

[0111]

(2) Preparation of spacer particles

5 parts by weight of the obtained seed particles of spacer particles was charged to a mixed aqueous solution comprising of 20 parts by weight of ion-exchanged water and 10 parts by weight of hydroxyethyl methacrylate and dispersed with a sonicater, and then the mixture was stirred uniformly. Then, a reaction system was replaced with a nitrogen gas and the mixture was stirred at 30°C for 2 hours. Then, to the reaction system was added 10 parts by weight of a 0.1 mol/liter aqueous solution of diammonium cerium nitrate ($[Ce(NH_4)_2](NO_3)_6$) regulated by a 1N aqueous solution of nitric acid, and after a polymerization reaction was conducted for 5 hours, a reactant was taken out and separated into particles and a reaction solution

through filtration using a 3 μm membrane filter. The obtained particles were adequately washed with ethanol and acetone and then dried under reduced pressure with a vacuum drier to obtain spacer particles, on the surface of which a vinyl-based thermoplastic resin is formed by graft polymerization.

[0112]

(3) Preparation of dispersion of spacer particles

The obtained spacer particles was taken by an amount required in such a way that a particle concentration is 0.3% by weight and gradually added to the medium comprising a mixture solution of 20 parts by weight of isopropyl alcohol, 60 parts by weight of ethylene glycol and 20 parts by weight of ion-exchanged water and dispersed uniformly by being adequately stirred with a sonicater, and then the resulting dispersion of spacer particles was filtered with a stainless screen with mesh size of 10 μm and cohesion spacers were removed to prepare a dispersion of spacer particles.

[0113]

(4) Preparation of substrate

The following three kinds of substrates were prepared using a color filter substrate, in which a black matrix of 15 μm in width was formed between pixels of a color filter and an ITO transparent contact electrode was formed on an overcoat provided on a color layer

1. Substrate A: An orientation layer comprising polyimide resin was uniformly formed on the whole area of the above-mentioned ITO transparent contact electrode of the color filter substrate. On this orientation layer, laser processing was applied in the form of stripe of 8 μm in width to the black matrix portion of the color filter as shown in Fig.2, and a surficial orientation layer (polyimide resin) was removed to prepare a substrate A exposing the ITO as a substrate. A contact angle θa of the

exposed ITO surface of the substrate A obtained relative to the dispersion of spacer particles obtained in a paragraph (3) was 25°, and a contact angle θb of the surficial orientation layer relative to the dispersion of spacer particles obtained in a paragraph (3) was 50°.

2. Substrate B: By applying a photosensitive polyimide resin precursor to the whole area of the above-mentioned ITO transparent contact electrode of the color filter substrate, exposing the photosensitive polyimide film through the medium of a mask and developing the film, a substrate B, in which in the black matrix portion of the color filter, an orientation layer comprising polyimide resin was not formed and the ITO as a substrate was exposed in the form of stripe of 8 μm in width, as shown in Fig.2, was prepared. A contact angle θa of the exposed ITO surface of the substrate B obtained relative to the dispersion of spacer particles obtained in a paragraph (3) was 25°, and a contact angle θb of the surficial orientation layer (polyimide resin) relative to the dispersion of spacer particles obtained in a paragraph (3) was 45°.

3. Substrate C: By following the same procedure as in the paragraph 1 except for not applying laser processing, a substrate C, in which an orientation layer comprising polyimide resin was formed on the whole area of an ITO transparent contact electrode, was prepared. A contact angle θb of the surficial orientation layer (polyimide resin) of the substrate C obtained relative to the dispersion of spacer particles obtained in a paragraph (3) was 50°.

[0114]

(Example 1)

A dispersion of spacer particles of 35 pL was ejected at 120 μm spacing onto the ITO surface (contact angle θa relative to the dispersion of spacer particles: 25°) in the

form of stripe on the substrate A (color filter substrate), which was exposed by applying laser processing, using an ink-jet system of a piezo ink-jet method, on which a head having a nozzle hole diameter of 30 µm is mounted, and then it was dried, and the spacer particles were located to prepare a substrate A (color filter substrate) in which the spacer particles were located. In addition, the spacer particle was adjusted and located in such a way that a distribution density of the spacer particles is 150 particles/mm^2. During locating the spacer particles, a substrate of room temperature was placed on a stage and the dispersion of spacer particles was ejected, the substrate, to which ejection of spacer particles was completed, was immediately shifted to on a hot plate heated to 90°C and dried. After visually recognizing that the medium was completely dried, the substrate was allowed to stand in an atmosphere of 90°C for 30 minutes and dried completely.

[0115]

Next, in order to bond a substrate (color filter substrate) in which the spacer particles were located to an opposed array substrate, a peripheral sealing material was printed by a screen printing method, and both substrates were bonded with this sealing material and then the sealing material was cured by heating at 160°C for 90 minutes to produce an empty cell with a cell gap of 5 µm. Then, a predetermined amount of liquid crystal for a TN type was filled into the empty cell by a vacuum method, and after a filling port was sealed with an end-sealing material, the end-sealing material was treated by heat at 120°C for 30 minutes to manufacture a TFT liquid crystal display.

[0116]

Display quality of the TFT liquid crystal display obtained above was evaluated. As a result, the existence of spacer particle was not found in a pixel area and no defects of display such as light leakage resulting from

abnormal orientation of liquid crystal in the vicinity of the spacer particle were found. Incidentally, the evaluation described above was conducted by visually observing the images magnified by an electron microscope with a voltage of 4.2 V applied.

[0117]

(Example 2)

By following the same procedure as in Example 1 except for using the substrate B (color filter substrate) as a substrate for locating the spacer particles and ejecting the dispersion of spacer particles onto the exposed ITO surface (contact angle θa relative to the dispersion of spacer particles: 25°) in the form of stripe on the substrate B (color filter substrate), a substrate B (color filter substrate) in which the spacer particles were located and a TFT liquid crystal display were manufactured.

[0118]

Display quality of the obtained TFT liquid crystal display was evaluated in the same manner as in Example 1. As a result, the existence of spacer particle was not found in a pixel area and no defects of display such as light leakage resulting from abnormal orientation of liquid crystal in the vicinity of the spacer particle were found.

[0119]

(Comparative Example 1)

By following the same procedure as in Example 1 except for using the substrate C (color filter substrate) as a substrate for locating the spacer particles and ejecting the dispersion of spacer particles onto the surface (contact angle θb relative to the dispersion of spacer particles: 50°) of the orientation layer (polyimide resin) on the substrate C (color filter substrate), a substrate C (color filter substrate) in which the spacer particles were located and a TFT liquid crystal display were manufactured.

[0120]

Display quality of the obtained TFT liquid crystal display was evaluated in the same manner as in Example 1. As a result, the existence of some spacer particle was found around a pixel area and light leakage resulting from abnormal orientation of liquid crystal in the vicinity of the spacer particle was found.

[0121]

[Effect of the Invention]

As noted above, if the method for manufacturing a liquid crystal display of the present invention is used, it is possible to locate the spacer particles selectively in a non-display area of the substrate with efficiency and high accuracy and to easily obtain a liquid crystal display which exhibits excellent display quality without the occurrence of a depolarization phenomenon resulting from the spacer particle and the reduction in contrast and color tone due to light leakage.

[0122]

Additionally the liquid crystal display of the present invention is preferably used in the method for manufacturing the liquid crystal display of the present invention. Furthermore if the method for manufacturing a liquid crystal display of the present invention is used, it is possible to obtain the liquid crystal display of the present invention easily.

[Brief Description of the Drawings]

[Fig. 1] A sectional view showing an example of a liquid crystal display.

[Fig. 2] A schematic view showing a position, where a spacer particle is located, on a substrate used in Examples 1 and 2.

[Description of the Symbols]

1 transparent substrate

2 polarizer

3 transparent electrode
4 color filter
5 black matrix
6 liquid crystal
7 spacer particle
8 orientation layer
9 sealing material

[Document Name] Abstract

[Abstract]

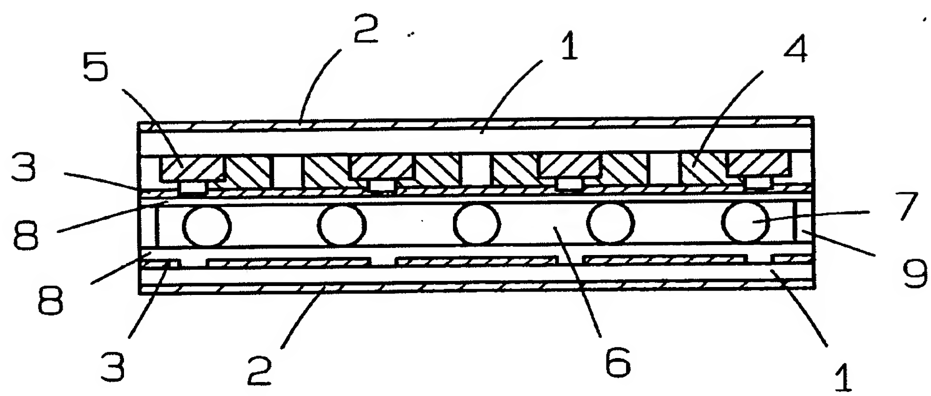
[Subject] To provide a method for manufacturing a liquid crystal display which exhibits excellent display quality without the occurrence of a depolarization phenomenon resulting from the spacer particle and the reduction in contrast and color tone due to light leakage caused by the spacer particles.

[Means for Solving] A method for manufacturing a liquid crystal display, which has a step ejecting a dispersion of spacer particles by an ink-jet device and a step setting a substrate having the spacers located at an arbitrary position and the other substrate having no spacer particle located on the opposite sides via the spacers and the liquid crystal, wherein a color filter comprising a pixel area arrayed in accordance with a given pattern and a shading area defining said pixel area is formed on one of the substrates, as a substrate to be located the spacer particles, a substrate, wherein an orientation layer, a contact angle of which relative to the dispersion of spacer particles is θb, is present in at least an area representing said pixel area on one side of the substrate and an area, a contact angle of which relative to the dispersion of spacer particles is θa, is present at least in a part of an area representing said shading area, and said θa and said θb satisfy θa < θb, is used and the spacer particles are selectively located in the shading area by ejecting a dispersion of spacer particles to a area, a contact angle of which relative to the dispersion of spacer particles is θa, of the substrate.

[Selective Figure] Non

[Document Name] Drawings

[Fig.1]



[Fig.2]